Message

From: Detlef Knappe [knappe@ncsu.edu]
Sent: 12/1/2017 11:33:59 PM
To: Strynar, Mark [Strynar.Mark@epa.gov]
Subject: [SPAM-Sender] Fwd: RE: GenX round 2
Attachments: HFPO Polymerization.pdf

Mark,

See below and attached.

Also, the initial motivation for Wellington to release HFPO-DA is (quote):

> Hexafluoropropylene oxide (HFPO) is a well-known versatile synthetic building block in the manufacturing of fluoropolymers (such as perfluoroalkoxy plastics) as well as a number of poly- and per-fluorinated intermediates. Although it is used to produce a vast number of commercial products, it's reactivity makes its survival in the environment unlikely. However, HFPO can react to form a stable dimer acid during oligomerization, or other manufacturing processes, which could lead to its detection in environmental samples. The presence of this HFPO dimer acid (HFPO-DA) in the environment could be due to residual leaching from commercial products or direct release during the manufacturing processes.
>
> For this reason, **Wellington** has synthesized a native and mass-labelled ($^{13}C_3$) hexafluoropropylene oxide dimer acid reference standard, **HFPO-DA** and **M3HFPO-DA** respectively, to aid researchers in their quantification of this potential environmental contaminant.

But it also seems that the probability of two HFPO molecules colliding in the atmosphere is low once leaving the stack. But it also sounds like Chemours is releasing much more HFPO than C3 dimer acid fluoride.

Detlef

-------- Forwarded Message --------
Subject: RE: GenX round 2
Date: Mon, 7 Aug 2017 15:50:52 +0000
From: Ryan, P Barry <bryan@emory.edu>
To: Detlef Knappe <knappe@ncsu.edu>
CC: Steenland, Kyle <nsteenl@emory.edu>

Detlef-

Sorry it took me a bit of time to get around to this- mostly because I misplaced the little piece of paper on which I had sketched out the mechanism. Please take a look at the attached PDF for the basic polymerization reaction. I would assume the monomers, dimers, trimers, tetramers, etc., would be hanging around, especially in environmental conditions where there was a lower concentration of HFPO meaning that a molecule of HFPO would not see another one very often and polymer terminating steps would be more likely to occur. Further, in any industrial process to produce HFPO, one might expect some contaminants that contain simple nucleophiles.

Perfluoro-2-methoxyacetic acid (CF3-O-CF2-COOH) is epoxide ring opening followed by oxidation in a related compound that has the epoxide attached to the terminal carbon. It is the monomer acid of that compound. CF3-O-CF2-O-CF2-COOH I, I believe, the dimer acid of the same compound.

Barry

P. Barry Ryan, Ph.D.

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From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Thursday, July 27, 2017 19:43
To: Ryan, P Barry <bryan@emory.edu>
Subject: Re: GenX round 2

Barry,

Not being an organic chemist, I am curious about the reaction mechanism that leads to HFPO dimer acid formation from HFPO. Is there a publication that depicts this pathway, or could you sketch it out for me? And does the reaction stop at the dimer acid or could there be a trimer with two ether bonds and a carboxylic acid at the end, etc.

Also, the dominant compound we see in the Cape Fear River is perfluoro-2-methoxyacetic acid (CF3-O-CF2-COOH). The second most dominant is CF3-O-CF2-O-CF2-COOH. Do you have any thoughts why these compounds might form, presumably as byproducts.

Best,

Detlef

On 7/6/17 11:31 AM, Ryan, P Barry wrote:

I am not at all sure what the "vinyl-ether process" might be- I would need som additional information. However, the dimer acid should form anytime HFPO is subject to any kind of nucleophilic attack, e.g., being in water where OH- is the nucleophile, of if some F- is floating around, e.g., HF in water. I expect that it is everywhere in these processes.

Barry

Sent from my iPhone

On Jul 6, 2017, at 11:23, Steenland, Kyle <nsteenl@emory.edu> wrote:

Thanks Detlef.

Serum samples do exist but I don't have straightforward access to them. I will contact Alan Ducatman about this, up at WVU, and see if there is any way to get them.

I am cc'ing my colleague (and chemist) Barry Ryan who worked on the C8 project with me, who may wish to chime in at some point.

In W Va, air deposition was important in getting the PFOA down to the groundwater, although it took years to leach through the soil Dupont's discharges of PFOA into the river were also important, as the river communicated with the ground water. In W Va, the drinking water all came though wells into the groundwater, not directly from the river.

Regards
Kyle

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Thursday, July 06, 2017 9:43 AM
To: Steenland, Kyle <nsteenl@emory.edu>; Jane Hoppin <jahoppin@ncsu.edu>
Cc: Rob Smart <rcsmart@ncsu.edu>; Collier, David <collierd@ecu.edu>; DeWitt, Jamie <DEWITTJ@ecu.edu>; Lea, Suzanne <LEAC@ecu.edu>; Katlyn May <kmay2@ncsu.edu>
Subject: Re: GenX round 2

I am not exactly sure at which point in their HFPO process the dimer acid forms. We do know that the dimer acid is present in the wastewater from the "vinyl-ether process" and that this wastewater, after some treatment, was discharged for 37 years into the Cape Fear River. In 2013, an abatement technology (we do not know what) was installed by Chemours that captured 80% of dimer acid according to Chemours (but we do not have any data to assess whether this is correct). So unabated wastewater discharges from 1980 to November 2013, then abated discharges from November 2013 until June 21, 2017. According to Chemours, wastewater from their vinyl ether process is now being diverted to onsite storage tanks and then taken by tanker truck to incineration facilities. So no more GenX/dimer acid discharges to the river since June 21, 2017. We are sampling to see how GenX concentrations are changing in the river. It is also important to note that GenX is only a small fraction (<1%) of the total fluorinated ether load that was entering the river. We do not know whether the new wastewater handling approach addresses GenX only or also the other ethers. Our sampling will answer that question as well. Almost nothing is know about the other ethers - are they by-products, produced for commercial intent? From which process line do they originate?

There are likely also HFPO and/or dimer acid emissions to the atmosphere (again, I don't know at which point the dimer acid forms). Mark Strynar and Andy Lindstrom have been finding the dimer acid in disconnected lakes and rivers near the Fayetteville works and also the Washington works (WV) plants. These results suggest that air deposition is also important. Air emissions likely have not stopped, but Chemours stated that they closed some vents in their process last month to help reduce air emissions. I think there is a very high likelihood that private wells have been contaminated in the vicinity of the Fayetteville works, similar to the groundwater contamination with PFOA in WV/OH. And GenX (or dimer acid) is likely present in the WV/OH groundwater.

Have serum samples from the C8 study been archived? Could one go back to some and see whether GenX and other ethers are present?

Detlef

On 7/6/17 9:11 AM, Steenland, Kyle wrote:

Thanks Detlef, that is clarifying.

When the HFPO gas forms the dimer acid, is that then a liquid? Is this process of dimerization taking place in the plant, and then the dimer acid is dumped into the river? If there any reason to believe they are no longer doing this, ie, no longer polluting the river with the dimer acid (GenX)?

Thanks
Kyle

Ps It appears from Sun et al. Figure 2 that there are a number of PFECAs besides GenX that are found in the water in quantities much greater than GenX. While I believe there is not much animal tox data on these chemicals, I would thing (based on the toxicology of GenX) that they would also be a cause of concern.

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Wednesday, July 05, 2017 11:10 PM
To: Steenland, Kyle <nsteenl@emory.edu>; Jane Hoppin <jahoppin@ncsu.edu>
Cc: Rob Smart <rcsmart@ncsu.edu>; Collier, David <collierd@ecu.edu>; DeWitt, Jamie <DEWITTJ@ecu.edu>; Lea, Suzanne <LEAC@ecu.edu>; Katlyn May <kmay2@ncsu.edu>
Subject: Re: GenX round 2

Kyle,

Chemours has two main production lines at the Fayetteville Works site. In one line, GenX is manufactured for commercial purposes, and Chemours captured all of the wastewater from this process and trucked it to Arkansas (and sometimes Ohio) for incineration. GenX, according to DuPont/Chemours is the trade name for the ammonium salt of this 6-carbon perfluorinated ether.

In the other line, they call it the vinyl-ether process, Chemours makes monomers for Teflon. One compound they are making is hexafluoropropylene oxide (HFPO). HFPO is a gas and is not stable. But it can form a dimer that Chemours/Dupont calls HFPO dimer acid or C3 dimer acid. This is the acid form of GenX, and DuPont/Chemours insists on not calling it GenX. But once in water, it's all the same, a 6-carbon ether carboxylate. Since the HFPO dimer acid is a by-product of the HFPO process, the wastewater from the HFPO process does not fall under the 99% capture requirement of the GenX consent order because by-products are exempt.

Happy to explain further.

Best,

Detlef

On 7/5/17 4:01 PM, Steenland, Kyle wrote:

Hmm, my understanding was the parent compound was never put in the river (at least legally, it was not permitted under the EPA agree in 2009 when they started making GenX), and that the GenX in the water was totally from legal discharge of other PFCs which formed GenX themselves, spontaneously - and which may have been happening since 1980. But I am certainly not sure about all this. I attach a recent news release which is not all that clear at the end (quotes from Chemours rep seem garbled) although it seems clear at the beginning. And another article along the same lines, a blog by a faculty member at UNC Wilmingon. Maybe Detleft can clarify.

Kyle

From: Jane Hoppin [mailto:jahoppin@ncsu.edu]
Sent: Wednesday, July 05, 2017 3:38 PM
To: Steenland, Kyle <nsteenl@emory.edu>
Cc: Rob Smart <rcsmart@ncsu.edu>; Detlef Knappe <knappe@ncsu.edu>; Collier, David <collierd@ecu.edu>; DeWitt, Jamie <DEWITTJ@ecu.edu>; Lea, Suzanne <LEAC@ecu.edu>; Katlyn May <kmay2@ncsu.edu>
Subject: Re: GenX round 2

Thanks Kyle,
So GenX the parent compound is no longer being released to the river, BUT GenX the byproduct is still being released from the air. I'm seeing if we can find well data for those living around Chemours, but we need to get that from the local health departments. So for now, I've focused on water from Wilmington.

Jane

On Wed, Jul 5, 2017 at 3:34 PM, Steenland, Kyle <nsteenl@emory.edu> wrote:

Looks better Jane. But I think you need to be clear about whether GenX is still being formed and still present in the drinking water. My understanding is that Chemours has stopped putting out the by-products from which the Gen X was being formed. Which would mean that serum levels will begin to drop, although not that quickly - but which in fact lends more urgency to collecting them now.

As far as the half life differing by age and gender, we found an age effect but not a gender one, for PFOA (attached). On the other hand we did not have children. And serum levels are higher in children than in adults.

Kyle

From: Jane Hoppin [mailto:jahoppin@ncsu.edu]
Sent: Wednesday, July 05, 2017 3:25 PM
To: Rob Smart <rcsmart@ncsu.edu>; Detlef Knappe <knappe@ncsu.edu>; Steenland, Kyle <nsteenl@emory.edu>; Collier, David <collierd@ecu.edu>; DeWitt, Jamie <DEWITTJ@ecu.edu>; Lea, Suzanne <LEAC@ecu.edu>; Katlyn May <kmay2@ncsu.edu>
Subject: GenX round 2

Hi all,

Thanks for your helpful comments on the first draft of the GenX proposal concept. This one I stripped down and am really focusing on the biological samples as well as the drinking water exposure.

Also stripped down to focus on GenX alone. I know you can measure more in the same analytical run, but easier to keep it focused.

I figure that we can afford to collect and measure samples from ~400 people, but have stated for now 200-400 because we need to do the formal budget to get that answer.

I kept in the clinical labs because they will be cheap and potentially of reassurance to the community.

When you look at this, please keep in mind that these are NOT the final specific aims, but rather a concept to run by NIEHS to make sure this is something they'd like us to pursue. I would like to send it to them tomorrow.

When I send to NIEHS, I will ask them if they want environmental samples collected as well. I think that's easy enough to do if we go to people's homes, more difficult if we're collecting biological samples elsewhere.

If you have been contacted by community members or regulators or anyone else about this, let me know. I'm not sure how I quantify that for the proposal, but it's worth keeping track of.

Thanks for your help.

Jane

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